Simulation of Confined Water in Equilibrium with a Bulk Reservoir

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The structural and dynamical properties of water in pores differ essentially from the bulk behaviour and depend strongly on the average water density in the pore, which is determined by the chemical equilibrium with the bulk reservoir. Simulations in the Gibbs ensemble offer the most direct way for the equilibration of coexisting phases.

In the present paper, Gibbs ensemble simulations were used for the equiliubration of water in spherical cavities with smooth surfaces and radii up to 20 Å and bulk liquid water at T = 300 K and P = 1 bar. Chemical equilibration between confined and bulk water was achieved by an essential number of molecule transfers. As the most important result we find that the liquid water starts entering the pore only if the water-pore interaction exceeds some critical value. Strengthening of the water-pore interaction causes an increase of the water density by more than 20%.

Analysis of the structural properties of the water in the pores shows the existence of two prominent outer water layers up to 7 Å from the pore surface. These layers exhibit strong orientational ordering. The pair correlation functions show evidence of a strong distortion of the tetrahedral structure in the first outer layer towards a square lattice arrangement. The diffusivity of water in the pore always decreases with respect to the bulk. Additionally, distributions of non short-circuted H-bond rings in confined and bulk water are analyzed.

The presented results show the applicability of Gibbs ensemble simulations for the equilibration of dense water systems. This offers new insights for the simulation of water in various confined environments in equilibrium with the water and also for simulations of other kinds of dense aqueous systems.